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HYDROCARBON LOSSES FROM VALVES AND
FLANGES

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Joint District, Federal and State Project for the
Evaluation of Refinery Emissions

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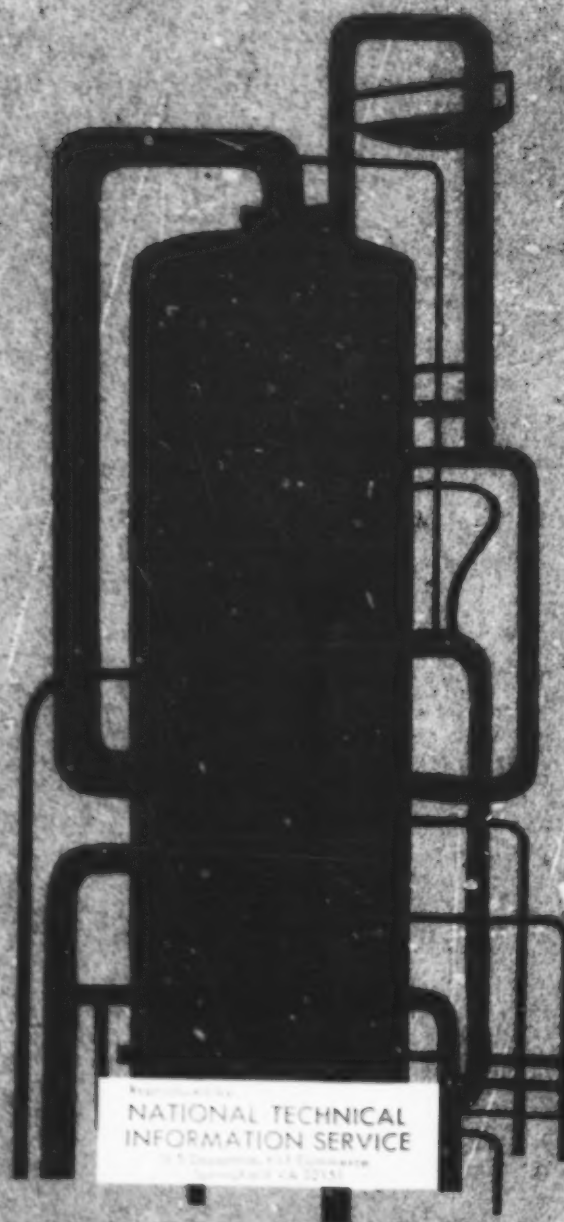
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FOR THE EVALUATION OF REFINERY EMISSIONS



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REPORT NUMBER 2

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this document may be better
studied on microfiche.

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HYDROCARBON LOSSES FROM VALVES AND FLANGES

IN BRIEF:

Hydrocarbon leaks from valves and flanges in refineries may be responsible for appreciable emissions to the atmosphere.

Questionnaires were sent out to obtain the number of valves and flanges, classified by service, in the refineries. A testing program was then initiated to obtain the leakage rates from a representative number of these units.

Tests indicated that flanges were of minor importance as sources of emissions, having approximately one-tenth the leak frequency of valves.

Nearly 10,000 valves were inspected, and the leakage was projected to the total population of 132,000 valves in Los Angeles County refineries. The calculated leakage was 7.5 tons per day of gaseous and 5.5 tons per day of liquid hydrocarbons, or a total of 13 tons per day of hydrocarbons from leaking valves in all the refineries.

It should be emphasized that not all of the 5.5 tons per day of liquid hydrocarbons escape to the atmosphere. An undetermined amount of this is ultimately recovered and returned to a process line.

HYDROCARBON LOSSES FROM VALVES AND FLANGES

Introduction

In 1955 a Joint District, Federal, and State Project was established to study the contribution of oil refineries to air pollution in Los Angeles County.

It is well known that flanged pipe connections and valves in refineries, under the influence of heat, pressure, vibration, friction, and the sometimes corrosive action of the products carried may develop leaks. Since undetected leaks exist, it was felt that a study should be conducted to determine their magnitude.

To aid in establishing a program for determining the losses from valves and flanges, questionnaires were sent to six major oil companies and five independent companies, stating in part:

"To expedite this survey, we request that you provide us with an estimate of the number of flanged connections and valve assemblies on piping in service for the two categories of petroleum products as follows:

1. Those with volatilities as high or higher than gasoline;
2. Those in the volatility range of kerosene, diesel, and stove oil."

In order to expedite the counting, it was decided that only the valves and flanges on pipelines one and one-half inches in diameter and larger should be reported.

After replies had been received from the oil companies, a sampling program was set up. Nine refinery areas were chosen which would include all the operations of all the refineries as follows:

- Area 1 - Crude Processing (including natural gasoline)
- Area 2 - Thermal Cracking and Visbreaking
- Area 3 - Catalytic Cracking and Reforming
- Area 4 - Catalytic Polymerization and Alkylation
- Area 5 - Gas Processing and Treating
- Area 6 - Liquid Product Treating
- Area 7 - L. P. G. Storage, Blending, and Shipping
- Area 8 - Product (other than L. P. G.) Storage, Blending, and Shipping
- Area 9 - Special Product Processing

Eight refineries were chosen for the tests, and the areas were assigned to various refineries so that each area was included in three different refineries. In each area chosen for testing, it was planned to inspect every sixth valve and every sixth flange for leakage and to measure the leakage rate from every leak found. The leakage data found were then to be projected to obtain the total leakage from all the refineries.

Testing Teams

The testing teams usually consisted of two or three men. One refinery employee, familiar with the unit and the products carried in the lines, accompanied the test team. One man recorded data while one or two other men inspected the valves and flanges.

Flanges

In the initial phase of the project, 129 flanges were inspected and only one was found to be leaking. An additional 197 flanges were later inspected and three were found to have slight leaks. Thus, out of 326 flanges, four leaks were found, three of them small leaks. As this was approximately one-tenth the leak frequency of valves and seemed to confirm the original belief that leakage from flanges was of minor importance, attention was directed toward valves only.

Valves

1. Procedure

It is first necessary to locate those valves that are leaking. Liquid leaks are found by observation; gaseous leaks by spraying the valves with soap solution and inspecting for the appearance of bubbles. (See Fig. 1.)

Liquid leaks are measured by collecting the liquid in a graduated cylinder for a convenient period of time and converting the results into milliliters per minute. If it is impossible to collect the liquid in a graduated cylinder, the number of drops per minute are counted. Twenty drops are considered to equal one milliliter.

For gaseous leaks, the valve is enclosed in a polyethylene bag. Glyptal cement is used to seal the edge of the polyethylene at the line of contact with the pipe. The cement is applied to the pipe and the edge of the bag is placed over it. Masking tape is then placed over the edge of the polyethylene and in contact with the pipe. A short length of 1/4 " I.D.

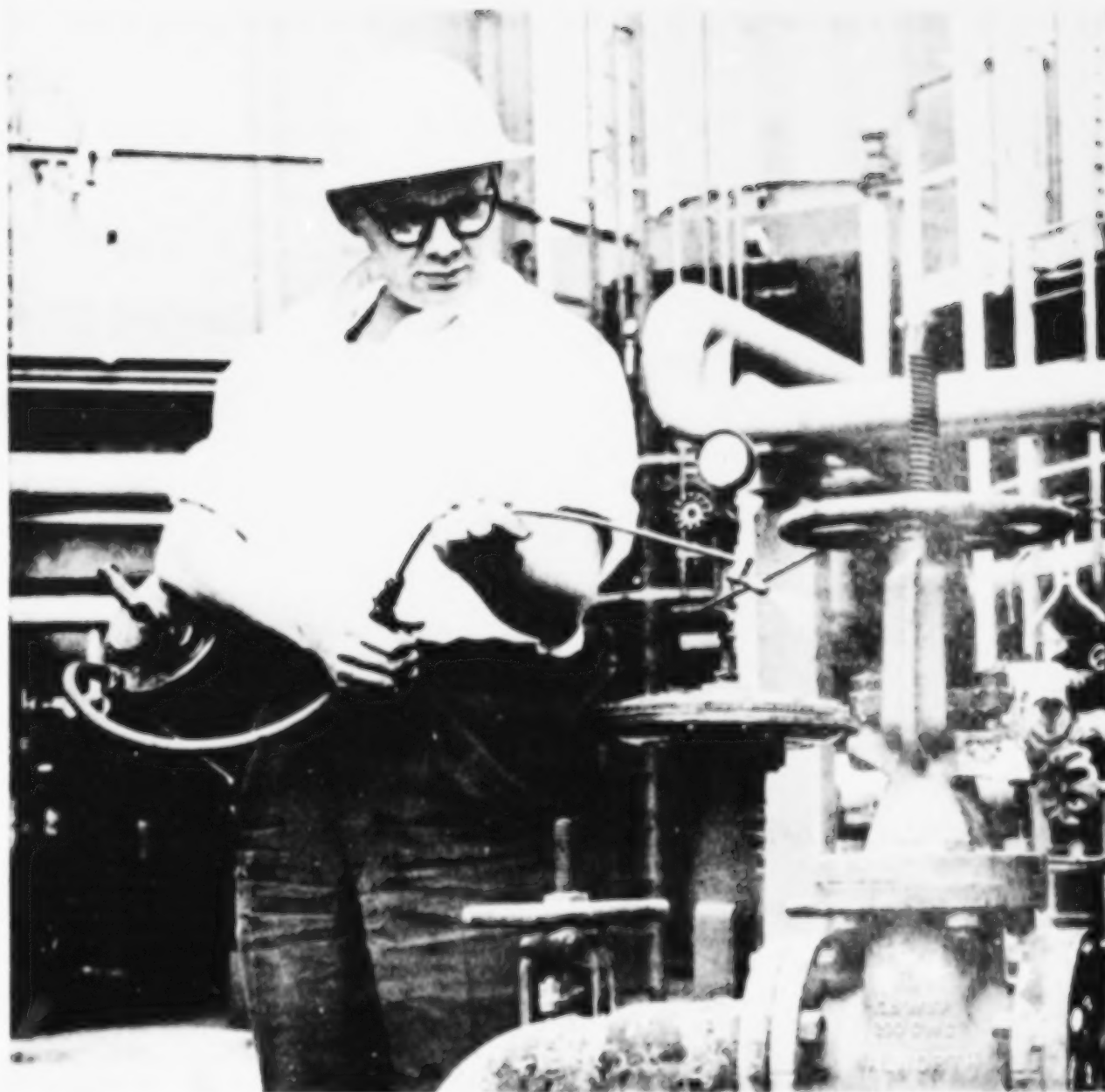


Fig. 1
Spraying Valve with Soap Solution

polyethylene tubing is sealed into a corner of the bag. A length of 1/4" I. D. rubber tubing is used to conduct the gas liberated at the leak from the polyethylene tubing to a wet test meter. (See Fig. 2.)

It is advisable to test the enclosure for leaks before attaching the rubber tubing to the meter by gently blowing back into the bag through the rubber tube. All seals are sprayed with soap solution so that leaks, if any, may be detected.

The system is allowed to reach a steady state and the rate of gas leakage is recorded. The temperature and pressure at the wet test meter are recorded. From the measured time interval and the wet test meter readings, the gas leakage rate is converted to standard cubic feet per hour (SCFH at 1 atm. and 60°F.).

2. Calculations

The weight per day of hydrocarbon vapor lost to the atmosphere from vapor leaks is found by the following equation:

$$\text{pounds per day} = \frac{(\text{SCFH}) (\text{mol. wt.})}{15.8}$$

For virtually pure gases, the molecular weight of the predominant gas was used. For mixtures, an attempt was made to use an "average" molecular weight, based on the plant foreman's estimate of the composition of the mixture.

The weight per day of hydrocarbons lost from liquid leaks is found by the following equation:

$$\text{pounds per day} = (\text{ml. per min.}) (\text{sp. gr.}) (3.16)$$

A value of 0.753 was used for the specific gravity in all calculations. This was considered to be a good average for most liquid hydrocarbons encountered.

3. Sampling Operations and Results

Originally it was planned to check every sixth valve for leakage and to measure the leakage from every valve found to be leaking in each refinery area chosen for surveying. Several survey visits were made using this scheme, but it was decided that it would be only slightly more difficult to check every valve for leakage and to measure the leakage from every sixth valve found to be leaking. Because of the ease of measuring liquid leaks, it was decided to measure every liquid leak found. For testing purposes, valves were divided into two main categories:

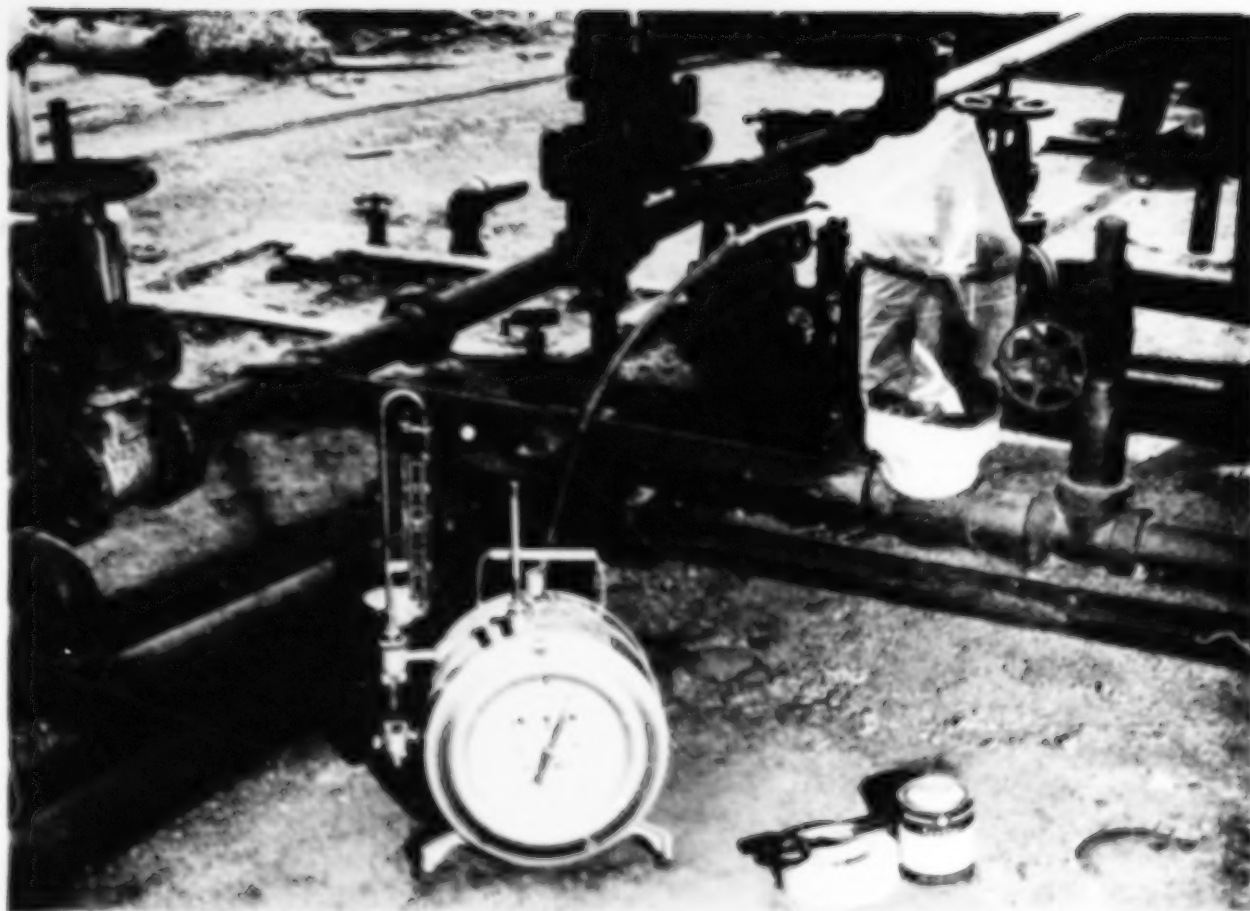


Fig. 2
Measurement of Valve Leak Rate

- a. Valves in hot lines (uncomfortably hot to the touch) and cold lines in liquid service:

These valves were not sprayed with soap solution, but were inspected for liquid leaks or (in the case of hot lines) for any visible mist from vaporized product. These hot vapor leaks could not be measured, nor could leaks of volatile liquids which ran down over the body of the valve but did not drip. Small leaks were, however, noted on the data sheets.

- b. Valves in cold lines (not uncomfortably hot to the touch) in gas service. This included vapor recovery systems and L.P.G. lines where the product would vaporize upon exposure to the atmosphere, even though it might exist as a liquid under high pressure in the line:

These valves were sprayed with soap solution and inspected for the appearance of bubbles. It was found that the rate of leakage could be estimated fairly closely in the range of 0.1 CFH (cubic feet per hour). Those estimated to be leaking at a rate of more than 0.1 CFH were noted as large leaks and every sixth one was measured as described previously. Those estimated to be leaking at a rate of less than 0.1 CFH were noted on the data sheets as small leaks. Proficiency in estimating the size of leaks by the rate of production of bubbles could only be gained by experience.

Questionnaires sent to six major oil companies and five independent companies elicited the information tabulated below:

<u>Company</u>	<u>High Volatility*</u>	<u>Low Volatility**</u>
A	10,000 valves	3,000 valves
B	8,246 "	4,105 "
C	9,200 "	2,860 "
D	8,774 "	1,866 "
E	7,600 "	2,600 "
F	5,700 "	3,000 "
G	4,325 "	1,300 "
H	776 "	160 "
I	702 "	178 "
J	715 "	150 "
K	600 "	200 "
Totals	56,638 valves	19,419 valves

*High volatility - volatility as high or higher than that of gasoline.

**Low volatility - volatility in the range of kerosine, stove oil, and diesel oil.

The above figures include only valves one and one-half inches in diameter and larger and do not include those carrying products below the volatility range of kerosine, diesel, and stove oil. In the field survey, however, all valves were inspected, including those less than one and one-half inches in diameter and those carrying products such as heavy gas oil, residuum, and asphalt. It was evident that the total number of valves of all sizes and services would have to be estimated in order to project the survey data to the total valve population.

The ratio of valves reported by the refineries to total valves could be calculated from the field survey data sheets, provided the data sheets listed the size and service of all valves inspected. These data were listed for most of the valves in gaseous service, but for only about 9.3 per cent of the valves in liquid service. In the initial phase of the project the size and service of each valve inspected was listed, but later, in the interest of conserving time, the non-leaking liquid valves were merely counted on a tally sheet and only leaking valves were listed on the data sheets.

Complete information (size and service) for each valve inspected was recorded for 2,237 valves in gas service and 674 valves in liquid service as shown below:

- a. Of 2,237 valves in gas service, 994 or 44.3% were one and one-half inches or larger in diameter.
- b. Of 674 valves in liquid service, 531 or 78.8% were one and one-half inches or larger in diameter.
- c. Of 674 valves in liquid service, 527 or 78.2% carried products with volatility as high or higher than that of kerosine, stove oil, or diesel oil.
- d. Of 9,521 valves inspected, 2,258 or 23.6% were in gas service, and 7,263 or 76.4% were in liquid service.

From the above, the total number of valves in all the refineries can be estimated.

23.6% of all valves are in gas service;

44.3% of these are one and one-half inches in diameter or larger.

Therefore, $23.6\% \times 44.3\%$, or 10.5% of all valves are in gas service and one and one-half inches in diameter or larger, and consequently were reported by the refineries.

76.4% of all valves are in liquid service;

78.8% of these are one and one-half inches in diameter or larger;

78.2% of these carry products with volatility as high or higher than that of kerosine, stove oil, or diesel oil.

Therefore, $76.4\% \times 78.8\% \times 78.2\%$, or 47.1% of all valves are in liquid service, are one and one-half inches in diameter or larger and carry products with volatility as high or higher than that of kerosine, stove oil, or diesel oil, and consequently were reported by the refineries.

$10.5\% \times 47.1\% = 57.6\%$ of all valves were reported by the refineries

$\frac{76,000}{0.576} = 132,000$ total valves of all sizes and all hydrocarbon services in all the refineries

It was originally planned to survey three refinery areas in each of eight refineries. This project was approximately one-third completed when a preliminary calculation indicated that the total hydrocarbon loss from valves would amount to about 15 tons per day; therefore, it was decided that the increased accuracy to be gained by following the original plan did not merit the additional time required. The results obtained in the survey are tabulated below:

	<u>Gas</u>	<u>Liquid</u>
Number of valves tested	2,258	7,263
Number of small leaks	256	768
Number of large leaks	118	79
Number of leaks measured	24	76
Total measured leakage, lbs./day	218	670
Expanded to include leaks not measured, lbs./day	1,072	708
Estimated loss from small leaks, lbs./day	26*	77*
Total estimated leakage, lbs./day	1,098	785

*Leaks too small to measure were estimated to have an average leakage rate of 0.1 pound per day. This is one-half the smallest measured leakage.

Of the 132,000 valves, 23.6% or 31,000 are in gas service. Projecting the gas leakage of 1,098 pounds per day from 2,258 valves to the total number of gas valves, the total gas leakage is calculated to be 15,000 pounds or 7.5 tons per day.

Of the 132,000 valves, 76.4% or 101,000 are in liquid service. Projecting the liquid leakage of 785 pounds per day from 7,263 valves to the total number of liquid valves, the total liquid hydrocarbon leakage is calculated to be 10,900 pounds or 5.5 tons per day.

The total leakage from 132,000 valves is calculated to be 13 tons per day.

4. Sources of Error

As in any procedure involving the projecting of a small number of tests to a large total population, certain possible errors are involved:

Eleven refineries reported a total of 76,000 valves, as tabulated on page 7. These process 95 per cent of the crude throughput of Los Angeles County. There are a few small refineries that do not process any crude oil, but it is estimated that the 11 refineries contain over 90 per cent of the valves in all the refineries in Los Angeles County. Any errors in the numbers of valves reported will, of course, be reflected by corresponding errors in the calculated total loss.

Wherever possible, every sixth large gas leak was measured. In some cases, however, the type or location of these valves, considerations of time, or some other factor, made this impossible. In those cases, the next leak found was measured.

The areas to be surveyed were not assigned to the refineries on a random basis. An effort was made to choose a refinery that had an "average" area with respect to size and age. It is believed by some that this method would result in greater accuracy than a strictly random assignment of areas to refineries.

In two refineries, three very large liquid leaks were found. If these three valves had not been leaking, the total liquid hydrocarbon loss calculated would have been 1.9 tons per day instead of 5.5 tons per day. When a very small number of samples exerts such a large influence on the final result, there is always a good possibility of a large error. The error, of course, may be in either direction.

In most refineries certain process areas are hosed down periodically and the water is conveyed to separators where oil is removed. It is impossible to estimate how much oil dripping from valves evaporates and how much is ultimately recovered and returned to a process line.

Small leaks were assigned a leakage rate of 0.1 pound per day. This is one-half the rate of the smallest measurable leaks. In many cases considerable mist was seen to be issuing from valves carrying hot liquid products, and these were considered to be small leaks.

Observations made while conducting the surveys and analysis of the results show that valve leakage from any given refinery area is largely a function of maintenance. It is also apparent that the standard of maintenance is fairly uniform throughout a given refinery. Since the valve project was not completed as originally planned, some refineries were not surveyed as extensively as others; the percentage of valves inspected in different refineries was not the same. As stated previously, the magnitude of the apparent leakage did not warrant the additional testing that would result in greater accuracy.

In gas service, 70 per cent of the measurable leaks are less than the average of 9.1 pounds per day. In liquid service, 90 per cent of the measurable leaks are less than the average of 8.8 pounds per day. This shows that the distribution of leaks is extremely skewed. Statistical analysis of the collected data would require special techniques and personnel which are not now available.

5. Discussion of Results

It seems evident that proper maintenance is the key to reducing losses due to leaks from valves and undoubtedly from other sources as well. Some companies have good maintenance programs, some poor, and the general quality of maintenance seems to extend throughout the particular refinery.

An example of low leakage rate was observed in one refinery where over 3,500 valves handling a wide variety of products under all conditions of temperature and pressure were inspected. The average leak rate was 0.038 pound per day per valve.

Examples of high leakage rates were found in two refineries where all 440 valves inspected in gas service had an average leak rate of 1.6 pounds per day per valve, and in one other refinery where all 1,335 valves inspected in liquid service had an average leak rate of 0.32 pound per day per valve.

These examples serve to illustrate the wide divergence from the average valve leak rate that can exist among refineries in a single area, subject to the same obligations to restrict their emissions to the greatest possible extent. The results could not be applied, even approximately, to refineries in other areas where the accepted standards are different.

Details of Valve and Flange Survey

1. Information from Refineries

In the planning stage of the project, it seemed logical to divide hydrocarbons into three classes according to their volatilities as follows:

- a. Those with volatilities as high or higher than gasoline.
- b. Those with volatilities in the range of kerosine, stove oil, and diesel oil.
- c. Those with volatilities below the range of diesel oil.

It was thought that Class a would be entirely lost to the atmosphere, Class b would be partly lost, depending on the individual condition, and Class c would be almost entirely absorbed into the ground or recovered and returned to the system. Thus, when the oil companies were asked to report the number of valves and flanges in their refineries, they were not asked to report those carrying Class c hydrocarbons.

In practice, however, the distinction is not so clear cut. For example, crude oil contains all three classes. In cracking processes, oil that goes into the unit as c comes out as a mixture of all three. In certain processes, absorbing oil c may contain up to 50 per cent or more of gaseous products that will flash off when reduced to atmospheric pressure.

The assumptions concerning the relative amounts lost are not entirely correct, either. In many cases leaks of gasoline are hosed down or allowed to drip into drains and are almost entirely recovered. In other cases leaks of c products contact hot pipes or hot equipment and most of the product evaporates, while the rest forms coke. Many cases have been seen where a coke deposit on a valve indicated a previous leak.

In calculating the total number of valves and total losses, the product breakdown provided by the oil companies was not used. Instead, the product breakdown was into gaseous and liquid products, based on the proportion of these valves inspected during the survey. In cases where both products were carried in a line, the product class was listed according to the predominant product. In such cases the valves were inspected for both liquid and gaseous leaks. No leaks of both gaseous and liquid products were found, but if there had been any, they would have been classified as both. It is obvious that only a portion of the liquid loss contributes to air pollution, but no attempt was made to estimate what that portion is due to lack of information upon which to base a valid estimate.

2. Equipment

For spraying valves with soap solution, an ordinary pressure type garden sprayer of approximately three-gallon capacity with an adjustable spray nozzle was used. For ease in carrying, it was seldom filled more than half full of an approximately 1 to 4 solution of liquid soap in water. The can could easily be carried by means of a shoulder strap, and the spray nozzle, connected to the can by a two and one-half foot hose, could be operated with one hand, leaving the other hand free for holding onto hand-rails or supports if necessary. For valves on tall towers, where carrying the spray can was cumbersome, a small plastic squeeze bottle filled with soap solution was used.

For measuring gaseous leaks, several sizes and shapes of polyethylene bags were used, depending on the size of the valves. Several one-hole rubber stoppers of various sizes with short lengths of glass tubing in the holes were used for lines open at one end where the valves leaked through the seat. Large size rubber tubing could sometimes be placed over the lines, as in the case of small sampling lines. Several lengths of polyethylene and rubber tubing, good quality masking tape, scissors, a can of Glyptal Number 1286 cement, a spatula for spreading the cement, and about 25 feet of light rope (for hoisting the gas meter up to places where it could not be carried) completed the small items needed. A wet test gas meter was used, but any meter capable of measuring gas at rates of 0.1 CFH to 20 CFH may be used.

For measuring liquid leaks, two graduated cylinders, 10-ml. and 100-ml. capacity, were used. The cylinders were flared at the top or were provided with a funnel to facilitate collection of the droplets.

3. Data Sheets

Figure 3 shows the data sheet used for recording field observations with some typical entries. Most of the column headings are self-explanatory, but mention will be made of some of them.

In column 1, the valves were numbered consecutively as they were inspected.

In column 4, any leaks noted were marked "S" if less than 0.1 CFH or too small to measure, or "L" if greater.

In column 6, products were classed as 1 (gaseous), 2 (liquids with volatilities as high or higher than kerosine), and 3 (liquids with volatilities less than kerosine).

In columns 7 and 8, temperatures were recorded as hot or cold and pressures were recorded if there was a pressure gauge on the line. This information was not used in the calculations.

In column 9, leaks were numbered consecutively as they were found.

As is mentioned elsewhere in the report, complete information was not recorded for all valves carrying liquid products, but only for those that leaked, except for 674 valves in liquid service inspected in the initial phase of the project. A tally of the valves inspected in each product class was kept on a separate sheet. Complete data must be kept on enough valves to obtain a good estimate of their distribution by size, product, etc., if this information will be needed later.

4. Notes to Testing Team

Plug (cock) valves usually have grease seals and must be inspected carefully. Seals not kept packed with grease may leak at high rates.

Leaks from pressure regulating valves cannot be measured by the technique described because of their size and shape and the fact that they have a compressed air tube coming out the top. Observations have shown that these valves seldom have large leaks.

Gas leaks through the seats of valves on sampling lines that point downward can be found by dipping the end of the line into a small beaker of water.

Gas leaks should be measured as they are found to prevent refinery maintenance operations from interfering with the performance of the tests.

Gas leaks in flanges are very difficult to find because the flange gaskets are usually recessed an inch or more inside the edges of the flanges, and soap bubbles, if any, are difficult to see.

It might be possible to measure hot vapor leaks by enclosing the valve loosely in a metal foil shroud, drawing air through the shroud at a measured rate, and measuring the concentration of gas or vapor in the air by some convenient means, as with a combustible gas tester. It might be assumed that liquid that condenses in the cool portion of this setup would condense in the air and not contribute to air pollution, or it might be possible to collect this liquid in a trap and measure it.